

# Solvent hydrodynamics affect crystal nucleation in suspensions of colloidal hard-spheres

Marc Radu<sup>1,2</sup> and Tanja Schilling<sup>1,\*</sup>

<sup>1</sup>*Theory of Soft Condensed Matter,*

*Université du Luxembourg, L-1511 Luxembourg, Luxembourg*

<sup>2</sup>*Institut für Physik, Johannes Gutenberg Universität, D 55099, Mainz, Germany*

## Abstract

Suspensions of colloidal hard particles are a well established model system to study fundamental questions of statistical mechanics experimentally and theoretically. Their popularity as a model system is partly due to the assumption that solvent effects on phase transition kinetics can easily be factored out – at least if one considers processes that are very slow compared to diffusive time-scales. In particular, crystal nucleation rates for hard sphere suspensions are often compared in units of a “typical” diffusion time.

Here, we present a study on the crystallization process in supersaturated suspensions of hard spheres, taking into account the solvent viscosity via hybrid dynamics simulations. We show that, although the induction times are long compared to the diffusion time, crystal nucleation rates still depend strongly on the solvent viscosity. We do not observe any differences in the sizes, shapes or structures of the nuclei that are formed. The effect is purely kinetic. As crystal nucleation kinetics are influenced non-trivially by hydrodynamic interactions, colloids might not be as ideal a model system to study phase transitions as has been assumed up to now.

Colloids are widely used as model systems to study fundamental questions of statistical mechanics. Over the past twenty-five years the phase behaviour, phase transition kinetics and glass transition of colloidal suspensions have been observed in numerous experiments and modelled by means of theory and simulations<sup>1–7</sup>. One reason the statistical mechanics community is interested in colloids, is that the interactions in colloidal suspensions can be tailored such that their equilibrium phase diagrams resemble those of atomic and molecular substances. Going beyond equilibrium physics, it is often suggested that also the phase transition behaviour on the colloidal scale should be similar to that on the atomic scale – at least in cases where excluded volume effects dominate the phase behaviour<sup>8–11</sup>.

However, while atoms and colloids resemble each other in many aspects, there is a major difference in their dynamics: Colloidal particles are suspended in a solvent. They interact directly with each other (e. g. by excluded volume) as well as indirectly by means of momentum transfer via the solvent. The latter phenomenon, called hydrodynamic interaction, is well known and thoroughly studied in the context of colloidal flow and sedimentation<sup>12</sup>. But when colloids are used as model systems for phase transition kinetics or for the glass transition, hydrodynamic interactions are usually neglected<sup>4,6,7,13</sup>.

In this article we would like to address the effect of the solvent on crystal nucleation in suspensions of colloidal hard spheres. We chose this system, because there has been a long-standing debate on the large differences in crystal nucleation rates that have been observed experimentally as well as by means of computer simulation<sup>14–18,19</sup>.

Experimentally, hard sphere suspensions are synthesized in various ways. Common systems are polystyrene spheres suspended in water, and sterically stabilized polymethylmethacrylate (PMMA) spheres in an organic liquid such as decalin. When a suspension is prepared for a crystallization experiment the static properties of the solvent are carefully adjusted (i. e. the density and the refractive index of the solvent are matched to those the colloidal particles), and the concentration is determined as accurately as possible. Transport properties such as the solvent viscosity, however, are hardly ever mentioned in publications on crystal nucleation in colloidal suspensions. There seems to be an underlying assumption, that crystallization

kinetics of chemically different systems can be compared (irrespective of solvent viscosity), as long as one uses a reduced time-scale – reduced with respect to a “typical” diffusion time.

There are several candidates for this time-scale. Some authors use the invers of  $D_0$ , the self-diffusion constant for an infinitely diluted system<sup>10,15,17,20</sup>. Other authors use the long-time self-diffusion constant of a colloid in the dense suspension  $D_L$ <sup>9,15,18</sup>. And in some studies the short-time diffusion constant  $D_S$  is used, which refers to time-scales, on which a particle interacts hydrodynamically but not directly with its effectively static neighbours<sup>8,16</sup>. In addition, often  $D_S$  and  $D_L$  are not measured directly, but inferred from  $D_0$  by means of two empirical relations:  $D_L/D_0 = (1 - \phi/\phi_g)^{2.57}$ , where  $\phi$  is the volume fraction of colloidal spheres in the system and  $\phi_g$  is their volume fraction at the glass transition<sup>9,15,21</sup>, and  $D_S/D_0 = (1 - \phi/\phi_{\text{rcp}})^{1.17}$ , where  $\phi_{\text{rcp}}$  is the volume fraction of spheres at random close packing<sup>21</sup>. We will present our nucleation rate data in terms of all three time-scales for comparison, and we will conclude that none of these time-scales suffices to factor out solvent effects.

We have simulated 8240 hard spheres suspended in a solvent at a volume fraction of  $\phi = 0.539$ . The solvent was modelled by means of multi-particle collision-dynamics<sup>22–24</sup> (see supplementary material for details). The starting configurations were prepared in the super-saturated liquid state and we verified that they did not contain crystalline precursors. Then we simulated 20-30 independent trajectories per value of viscosity until crystallization was reached in all cases. Despite the relatively high packing fraction, we observe an induction period that is long compared to the diffusion times of the system followed by a regime of rapid growth (see crystallization curves in the supplementary material). We did not use any rare event sampling scheme to speed up sampling, as we did not wish to make any assumptions on the evolution of the density of states or the length of correlation-times involved in the process.

We present all data in units of the sphere diameter  $a$ , the mass of a sphere  $m$  and the thermal energy  $k_B T$ . Solvent viscosities ranged between  $4 \sqrt{mk_B T}/a^2$  and  $70 \sqrt{mk_B T}/a^2$ . Translated to an experimental system with colloidal particles of radius  $\sim 420 \text{ nm}$  suspended in a solvent

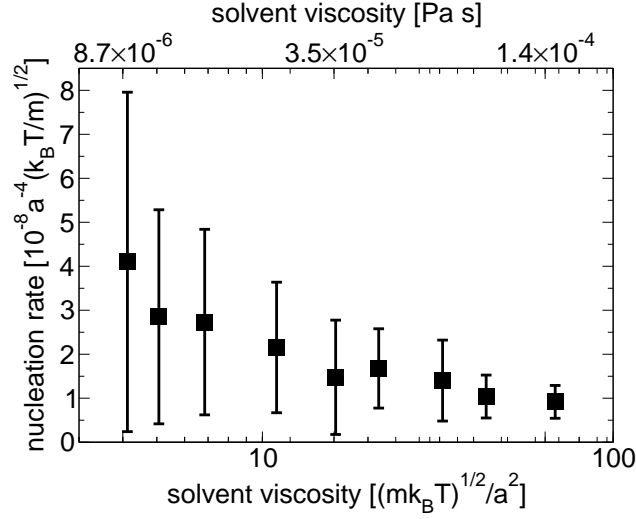


FIG. 1. Nucleation rates as a function of solvent viscosity.

of mass density  $\sim 1 \text{ kg m}^{-3}$  at room temperature, these viscosities correspond to a range of  $8.9 \cdot 10^{-6} \text{ Pa} \cdot \text{s}$  to  $1.5 \cdot 10^{-4} \text{ Pa} \cdot \text{s}$ . For higher viscosities (up to  $2 \cdot 10^{-3} \text{ Pa} \cdot \text{s}$ ) we simulated the diffusion behaviour, but not the crystallization process because the induction times became forbidding long.<sup>25</sup>

Fig. 1 shows the nucleation rate versus viscosity. The rate drops with increasing viscosity, because the colloids' diffusive motion slows down. The question is, whether it is possible to rescale the data with respect to the diffusion time such that it collapses onto one value.

Fig. 2 shows the dependence of the diffusion times on viscosity. We obtained  $D_0$  by means of a fit to the mean squared displacement of a single particle in the infinitely dilute solvent. To determine  $D_L$  and  $D_S$  we recorded the mean squared displacement of a particle in the supersaturated melt. There was a clear diffusive regime at long times to which  $D_L$  could be fitted. However, even at viscosities that correspond to the range that is commonly used in experiments, there was no short-time diffusive regime (for details see supplementary material). We therefore resorted to using the maximum value of the time-integral over the velocity-velocity autocorrelation function<sup>26</sup> and called it a “short-time diffusion constant”, although, strictly speaking, it does not correspond to diffusive motion (see supplementary material).

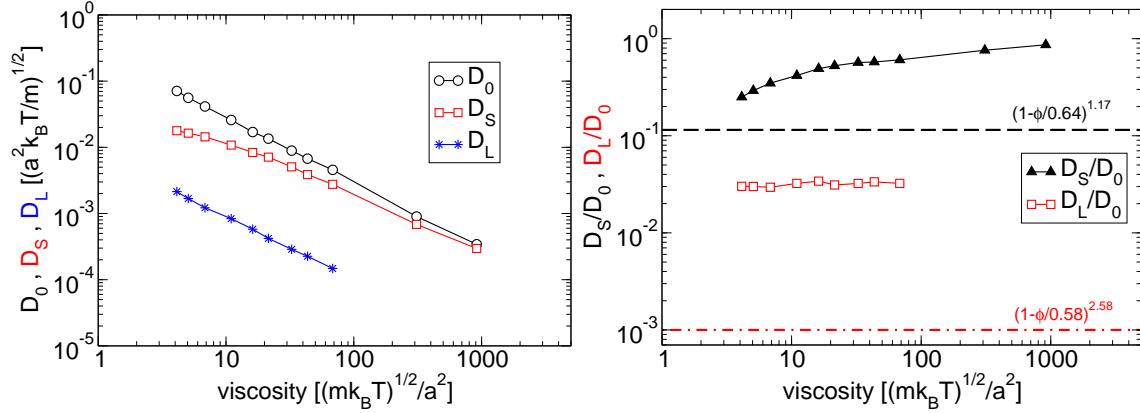


FIG. 2. Diffusion constants versus viscosity. Left: Absolute values for  $D_0$  (circles),  $D_S$  (squares) and  $D_L$  (stars), Right: Ratios  $D_S/D_0$  (triangles),  $D_L/D_0$  (squares) and expressions according to ref.<sup>9,21</sup>.

The left panel of Fig. 2 shows the absolute values of the diffusion constants, the right panel their ratios in comparison to the power laws that are commonly used to estimate them. Clearly, the system is not concentrated enough for these asymptotic expressions to hold. Nevertheless they have been applied at even lower packing fractions in various studies on crystal nucleation in the past<sup>8,15,16</sup>.

Fig. 3 shows the nucleation rates rescaled with respect to  $D_L$  and  $D_0$ . They clearly depend on viscosity. Thus nucleation rates measured in suspensions of hard spheres with different solvent viscosities cannot be simply superposed by means of a rescaling with respect to  $D_0$  or  $D_L$ ; crystallization kinetics is clearly influenced by solvent hydrodynamics beyond the level of diffusion.

The lower panel of fig. 4 shows the nucleation rates re-scaled with respect to  $D_s$ . At first glance, one might conclude, that this time-scale is the proper choice. However, fig. 4 upper panel shows a test of this hypothesis for another value of supersaturation ( $\phi = 0.544$ ). The collapse of the data at  $\phi = 0.539$  is a pure coincidence.

If the nucleation rates depend on viscosity, one could expect to observe differences in the sizes, shapes or structures of the crystallites that form, too. We analysed the structures of the

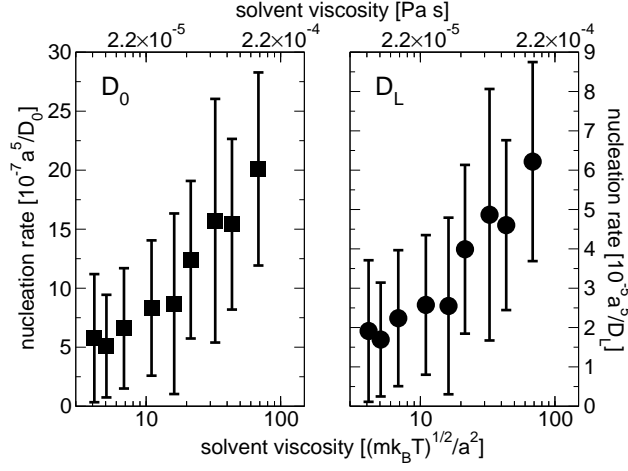


FIG. 3. Nucleation rates scaled by  $D_0$  (left panel) and  $D_L$  (right panel) as a function of solvent viscosity. Both graphs show that the nucleation kinetics change with viscosity beyond the trivial dependence of diffusion times.

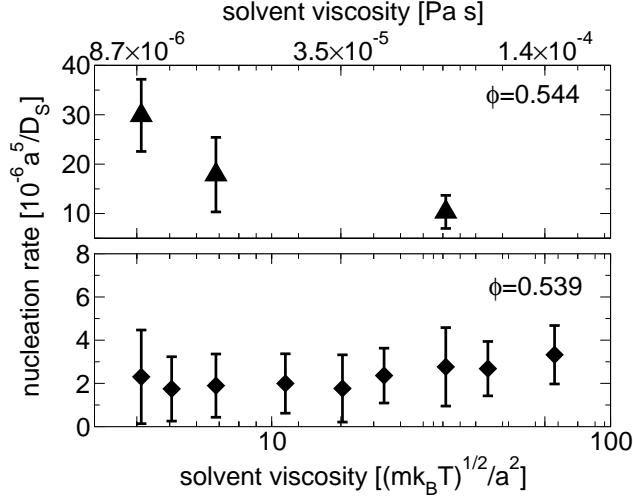


FIG. 4. Nucleation rate normalized with respect to the short-time diffusion constant  $D_s$  for  $\phi = 0.539$  (lower panel) and  $\phi = 0.544$  (upper panel)

growing crystallites in terms of their q6q6-bond-order<sup>27,28</sup>. Comparing clusters of equal sizes from trajectories at different viscosities, neither the radii of gyration nor the distributions of q6q6-values differed within the statistical accuracy. We performed a committor analysis for the highest and the lowest viscosity and did not find any difference in the critical cluster

size, shape or structure, either. Thus we conclude that the effect we observe is purely kinetic.

In summary, we have simulated crystallization of a supersaturated suspension of hard spheres fully taking into account the solvent hydrodynamics. We find that kinetics need to be taken with care when one studies phase transitions in colloids. The crystallization process in hard sphere suspensions is richer than has been suggested in the literature so far. There is a clear dependence of the nucleation rates on viscosity beyond the trivial slowing down of diffusion. However, the crystal structure and shape of the critical nucleus seem to be independent of viscosity, hence what we have described here is a purely dynamical effect. In addition we showed that there is no clear short-time diffusive regime for the concentrations and viscosities commonly used in experiments. And that the power laws that are often used to infer diffusion constants do not hold for the volume fraction at which one usually studies nucleation.

## METHODS

### *SIMULATION METHOD*

To simulate hard spheres suspended in a liquid, we used a combination of an event-driven molecular dynamics (EDMD) algorithm<sup>29–32</sup> for the spheres and multiparticle-collision dynamics (MPCD)<sup>22,23</sup> as a mesoscopic solvent model to account for the hydrodynamic interactions. The basic idea of a MPCD algorithm is to transport momentum through the system by means of  $n$  point particles of mass  $m$  while satisfying the conservation laws of mass, energy and momentum locally. The algorithm consists of two steps, namely free streaming interrupted by multiparticle collisions. In the streaming step, all fluid particles are propagated ballistically with their velocities  $\mathbf{v}_k$ , i.e. the particle positions are updated according to a time increment  $h$  as

$$\mathbf{x}_k(t+h) = \mathbf{x}_k(t) + h\mathbf{v}_k(t). \quad (1)$$

After the time step  $h$ , the  $n$  fluid particles are sorted into a lattice of cubic cells of size  $a \times a \times a$ , such that on average  $\bar{n}$  particles are within each collision cell. Then, the particle

velocities are rotated around the center of mass velocity  $\bar{\mathbf{v}}$  in this cell,

$$\mathbf{v}_k(t+h) = \bar{\mathbf{v}}(t) + \underline{\Omega}(\alpha) [\mathbf{v}_k(t) - \bar{\mathbf{v}}(t)], \quad (2)$$

where  $\underline{\Omega}(\alpha)$  is a rotation matrix corresponding to a fixed angle  $\alpha$ , which is generated randomly for each cell. Before a collision step is carried out, the collision cell grid is shifted by a randomly chosen vector with components taken from the interval  $[-a/2, a/2]$ , to ensure Galilean invariance<sup>24</sup>. Here, we realized coupling between the colloidal particles and the “solvent” particles in the simplest manner, i. e. the colloid takes part in the collision step eq. 2 as a point particle with instantaneous velocity  $\mathbf{V}$  and mass  $M$  within its cell with  $\bar{\mathbf{v}} = (M\mathbf{V} + m \sum^n \mathbf{v}) / (M + nm)$ .

In order to measure the solvent viscosities we imposed a Poiseuille flow between two planar walls. From the resulting parabolic velocity field we extracted  $\eta_0$  from  $v_{\max}$ .

## *SIMULATION DETAILS*

We simulated 8240 hard spheres suspended in a solvent at volume fractions of  $\phi = 0.539$  and  $\phi = 0.544$ . The starting configurations were prepared in the supersaturated liquid state and we verified by means of bond-order analysis that they did not contain crystalline precursors. We simulated 20-30 independent trajectories per value of viscosity until crystallization was reached in all cases. The simulations were run in an unbiased way, i. e. we did not enhance statistics by any type of rare event sampling method.

## *ANALYSIS*

### Nucleation Time

We identified crystallites by means of the “q6q6-bond order parameter”<sup>27,28</sup>. Fig 5 shows the number of particles in the largest crystalline cluster versus time for two typical crystallization runs – one at a low viscosity and one at a high viscosity. The crystallization process clearly



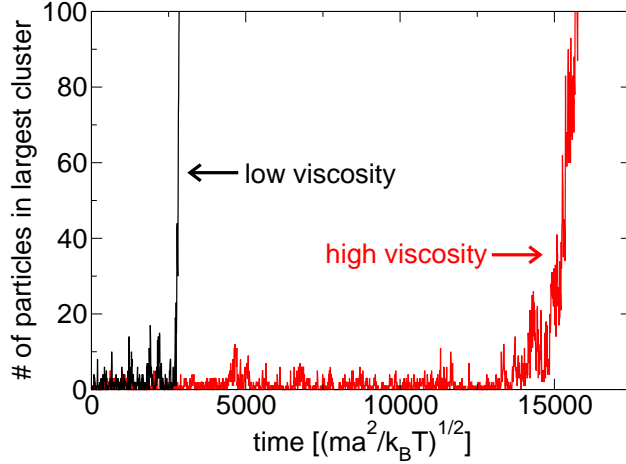


FIG. 5. Number of particles in the largest cluster as a function of time for one trajectory at a low value of solvent viscosity and one at a high value.

consists of a very long induction time followed by a fast event. Hence, even though the packing fraction is too high to expect classical nucleation theory to hold, we are still dealing with an activated, rare event.

Once a run had produced a cluster of more than 80 particles, it definitely crystallized. Thus we used this value to locate the nucleation time. To test the validity of this criterion, we performed a commitor analysis for two values of viscosity ( $\eta = 4.17(mk_BT)^{1/2}/a^2$  and  $\eta = 63.93(mk_BT)^{1/2}/a^2$ ). We found that a cluster size of ca. 30 particles corresponds to a 50% probability for subsequent full crystallization in both cases.

As the average induction time we took the arithmetic mean of the distribution of measured induction times, and its standard deviation to determine the error bars. The nucleation rate is then given by

$$I = \frac{1}{V \langle t_{\text{ind}} \rangle} \quad ,$$

where  $V$  is the volume of the system.

#### Diffusion constants

To determine  $D_0$  we computed the mean squared displacement of a particle in the infinitely dilute solution versus time and fitted a straight line to it. (The result was consistent with

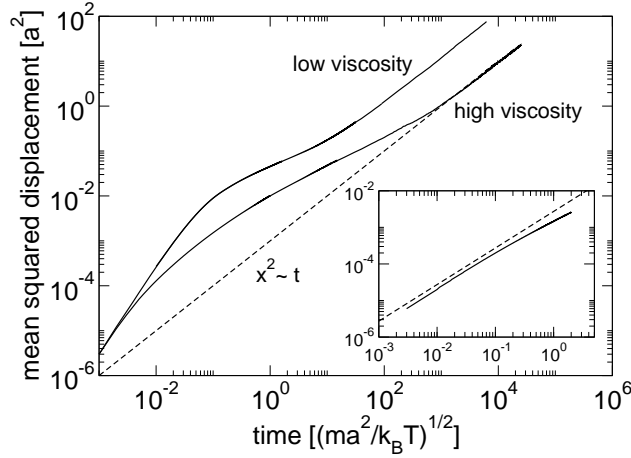


FIG. 6. Mean squared displacement of a particle in the suspension versus time for  $\eta = 4.17(mk_BT)^{1/2}/a^2$  and  $\eta = 63.93(mk_BT)^{1/2}/a^2$  (main panel) and  $915\sqrt{mk_BT}/a^2$  (inset). Even at  $915\sqrt{mk_BT}/a^2$  which corresponds to  $2 \cdot 10^{-3} Pa \cdot s$  there is no short-time diffusive regime.

the shear viscosity  $\eta_0$  that we had measured independently, see above. I.e. the Stokes-Einstein relation was fulfilled.)  $D_L$  was determined by means of a fit to the mean squared displacement of a particle in the dense solution (see fig. 6). Even for the highest viscosity we simulated, which corresponds to the viscosity of a typical experiment on hard sphere crystallization, we did not see a short time diffusive regime.

In order to obtain a value for  $D_S$ , nevertheless, we tried two other approaches: we fitted the dynamic structure factor, but the results depend strongly on the choice of time-window for the “short-time” regime. And we computed the time-integral over the velocity-velocity autocorrelation function, as suggested in ref.<sup>26</sup>

$$D(t) = \frac{1}{3N} \sum_{i=1}^N \int_0^t dt' \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t') \rangle, \quad (3)$$

and identified its maximum value with  $D_S$  (see Fig. 7). This approach turned out to be relatively robust.

### Structure of Crystallites

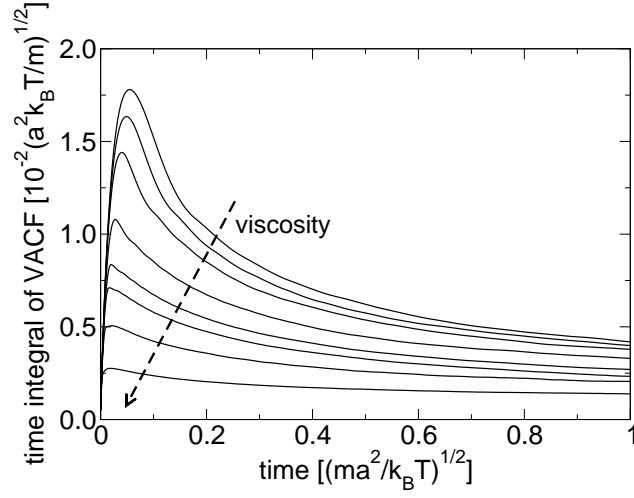


FIG. 7. Measured time integrals over velocity velocity autocorrelation function. The maxima were taken for  $D_S$

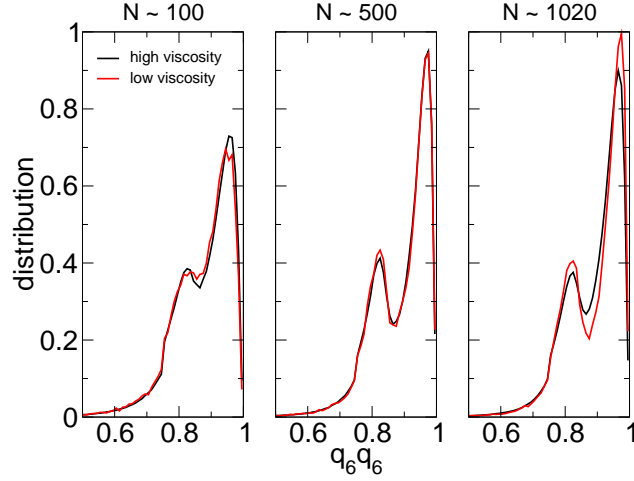


FIG. 8. Distributions of  $q_6 q_6$  for different sizes of the largest cluster. Here shown for small and high viscosity.

To check if the structure of the crystallites depends on viscosity, we computed the  $q_6 q_6$  distributions for clusters of equal sizes at different viscosities. Fig. 8 shows that the crystallites are very similar in structure. The snapshots figs. 9, 10 do not allow for a distinction between low and high viscosity, either.

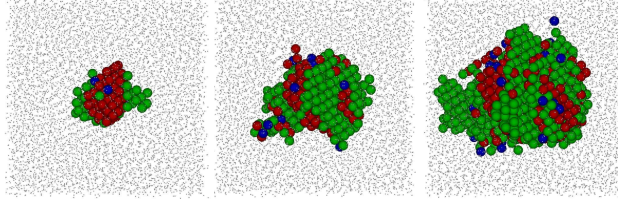


FIG. 9. Timeseries of snapshots of the largest cluster for small viscosity.

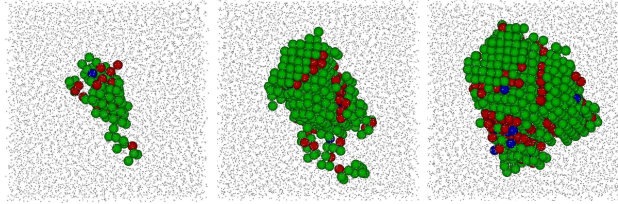


FIG. 10. Timeseries of snapshots of the largest cluster for high viscosity.

---

\* tanja.schilling@uni.lu

<sup>1</sup> H. Lowen, Physics Reports-Review Section of Physics Letters **237**, 249 (1994)

<sup>2</sup> T. Palberg, JOURNAL OF PHYSICS-CONDENSED MATTER **11**, R323 (JUL 19 1999), ISSN 0953-8984

<sup>3</sup> W. Poon, JOURNAL OF PHYSICS-CONDENSED MATTER **14**, R859 (AUG 26 2002), ISSN 0953-8984

<sup>4</sup> V. J. Anderson and H. N. W. Lekkerkerker, Nature **416**, 811 (2002)

<sup>5</sup> A. Yethiraj, SOFT MATTER **3**, 1099 (2007), ISSN 1744-683X

<sup>6</sup> U. Gasser, Journal of Physics-Condensed Matter **21** (2009)

<sup>7</sup> G. L. Hunter and E. R. Weeks, Reports on Progress in Physics **75** (2012)

<sup>8</sup> Y. M. He, B. J. Ackerson, W. van Megen, S. M. Underwood, and K. Schatzel, Physical Review E **54**, 5286 (1996)

<sup>9</sup> J. L. Harland, S. I. Henderson, S. M. Underwood, and W. Van Megen, Physical Review Letters **75**, 3572 (1995)

- <sup>10</sup> S. Iacopini, T. Palberg, and H. J. Schope, *Journal of Chemical Physics* **130** (2009)
- <sup>11</sup> W. C. K. Poon, E. R. Weeks, and C. P. Royall, *Soft Matter* **8**, 21 (2012)
- <sup>12</sup> R. S., *Adv. Phys.* **50**, 297 (2001)
- <sup>13</sup> H. Lowen, *Journal of Physics-Condensed Matter* **21** (2009)
- <sup>14</sup> K. Schatzel and B. J. Ackerson, *Physical Review E* **48**, 3766 (1993)
- <sup>15</sup> J. L. Harland and W. van Megen, *Physical Review E* **55**, 3054 (1997)
- <sup>16</sup> S. Auer and D. Frenkel, *Nature* **409**, 1020 (2001)
- <sup>17</sup> L. Filion, R. Ni, D. Frenkel, and M. Dijkstra, *Journal of Chemical Physics* **134** (2011)
- <sup>18</sup> T. Schilling, S. Dorosz, H. J. Schöpe, and G. Opletal, *Journal of Physics: Condensed Matter* **23**, 194120 (2011), <http://stacks.iop.org/0953-8984/23/i=19/a=194120>
- <sup>19</sup> One source of this discrepancy is the difficulty to control the concentration of colloids<sup>11</sup>. This effect, albeit very important, is one of experimental accuracy rather than of the underlying physics. The effect of hydrodynamic interaction which we discuss here, however, stems from a misunderstanding regarding the dynamics of the system.
- <sup>20</sup> U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, and D. A. Weitz, *Science* **292**, 258 (2001)
- <sup>21</sup> J. van Duijneveldt and H. Lekkerkerker, in *Science and Technology of Crystal Growth*, edited by J. van der eerden and O. Bruinsma (Kluwer Academic Publishers, 1995) p. 279
- <sup>22</sup> A. Malevanets and R. Kapral, *Journal of Chemical Physics* **110**, 8605 (1999), malevanets, A Kapral, R
- <sup>23</sup> A. Malevanets and R. Kapral, *Journal of Chemical Physics* **112**, 7260 (2000), malevanets, A Kapral, R
- <sup>24</sup> T. Ihle and D. M. Kroll, *Physical Review E* **63**, art. no. (2001), ihle, T Kroll, DM Part 1
- <sup>25</sup> Typical experimental viscosities range between  $1 \cdot 10^{-3} Pa \cdot s$  and  $3 \cdot 10^{-3} Pa \cdot s$  – i.e. we have not quite reached these values with our nucleatun runs. But none of the results that we present in the following shows any levelling off with increasing viscosity. Hence it is very likely that our conclusions hold for the solvents that are commonly used in experiments, too.
- <sup>26</sup> A. Tomilov, A. Videoq, T. Chartier, T. Ala-Nissila, and I. Vattulainen, *Journal of Chemical Physics* **137** (2012), tomilov, A Videoq, A Chartier, T Ala-Nissila, T Vattulainen, I

- <sup>27</sup> P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (Jul 1983)
- <sup>28</sup> P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, Phys. Rev. Lett. **75**, 2714 (Oct 1995)
- <sup>29</sup> B. J. Alder and T. E. Wainwright, The Journal of Chemical Physics **31**, 459 (1959)
- <sup>30</sup> M. Marin and P. Cordero, Computer Physics Communications **92**, 214 (1995), mARIN, M CORDERO, P
- <sup>31</sup> A. Krantz, ACM Transaction on Modeling and Computer Simulations **6**, 185 (1996), a.T. Krantz
- <sup>32</sup> B. D. Lubachevsky, Journal of Computational Physics **94**, 255 (1991), IUBACHEVSKY, BD

## ACKNOWLEDGMENTS

We thank William van Megen, Peter Pusey, Hajime Tanaka, Hajo Schöpe and Tobias Kraus for providing us with data on solvent viscosities. This work has been supported financially by the German research foundation (DFG) within SFB TR6. The present project is supported by the National Research Fund, Luxembourg